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(54) Title: POLYMER COATED POWDERS (57) Abstract A process for coating a solid with a water-insoluble or slightly water-soluble coating material consisting essentially of a high-viscosity polymer and/or wax and/or grease, or mixtures thereof, comprises dissolving the said coating material in one or more materials selected from among carboxylic acids, carboxylic acid anhydrides, carboxylic acid halides and/or mixtures thereof, to form a low-viscosity "polymer solution", contacting the solid to be coated with the said "polymer solution", and chemically or physically modifying the "polymer solution" to cause the formation of a coating of increased viscosity.		

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POLYMER COATED POWDERS

Field of the Invention

The present invention relates to a novel process for coating inorganic and organic solids with polymers, waxes and greases, at a temperature lower than the softening temperature of the original raw materials that constitute the coating. This process is particularly important for the preparation of surface coated powders of organic and inorganic materials such as Al, Cu, MgO, talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , $\text{Ca}(\text{OH})_2$, TiO_2 , Al_2O_3 , SiO_2 , CaSO_4 , $\text{Al}(\text{OH})_3$, cellulose fibers, paper, glass fibers, alumina fibers, whiskers and platelets, SiC fibers, whiskers and platelets, TiN fibers and whiskers, other ceramic powders in the form of oxides, carbides and nitrides, and mixtures thereof. Also, it is an important process for the preparation of surface coated fertilizers, to prevent their caking and/or turn them into slow release fertilizers such as KNO_3 , KCl , $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, urea, etc. and mixtures thereof.

The present invention relates to a method for the production and uses of materials coated with polymers, waxes or greases. The invention makes it possible to produce powders of improved performance and compatibility with a variety of other materials, namely, minerals, plastics and cellulose, and lowers the cost of their production. This invention makes it also possible to glue two or more different materials together in an unconventional and inexpensive manner.

The present invention is particularly important, inter alia, in the fertilizers industry and in the production of powders for the cement (construction) industry, for the paper industry, for the textile industry, for the cosmetics industry, for the adhesives industry, for the paint industry, for the ceramic industry, for the plastic and rubber industries, etc.

Background of the Invention

Application of Surface-Modified Powders

The literature is replete with patents, articles, reviews and books concerning the production and beneficiation of minerals (e.g. "Mineral Processing"; E. J. Pryor; Elsevier Publishing; Third Ed.; 1965) and their uses, especially after surface modifications, in the plastics compounding, in the paper industry, in the ceramic industry, in the paint industry, etc. (e.g. "CaCO₃ Fillers - Market Trends and Developments"; J. Revert'e i Vidal; Industrial Minerals; November 1994, "Plastic Compounding - Where Mineral Meets Polymer"; M. O'Driscoll; Industrial Minerals; December 1994, "Surface Modification of Mineral Fillers"; R. Goodman; Industrial Minerals; February 1995, "Magnesium Hydroxide Flame Retardant (NHFR) for Plastics and Rubber"; O. Kalisky et al; Chimica Oggi/Chemistry Today; June 1995 and references therein). The above reviews illustrate the importance of the physical properties, and especially the surface characteristics, of fine powders that are used in a large variety of applications.

Size Reduction

Powders are intensively used in numerous applications, e.g. fillers and flame retardants in the paper and in the plastics industries, as raw materials for ceramics and cements, as constituents in cosmetics, etc.. In order to make effective use of powders, their particle size distribution should be controlled, usually reduced, and their surface properties should be compatible with those of the substrates with which these powders are to be used.

Grinding or milling of materials are common technologies for size reduction. However, they require the expenditure of high energies, especially in the sub-micron range, at which the high surface area of the particles increases the rate of their coalescence. The

high cost of such operations is increased by their low productivity and by the requirement for equipment made of special materials that withstand the high attrition and minimize the contamination of the final fine powders. Generally, two processes are used in the art - dry and wet grinding/milling. In order to increase the production rates of both types of processes and to afford better qualities of grinding/milling, aids, such as dispersants like sodium hexametaphosphate, etc., are usually employed.

Another approach for obtaining fine powders involves their controlled recrystallization or precipitation by reacting suitable reactants.

In the cases described above, it is of great importance that any slurry of fine powders be stable, namely, that the fine particles will not undergo coalescence and the solids will not separate or precipitate even after long periods of time. Also, it is required that the final dry fine powders be free flowing. This can be achieved, among other methods, by coating the fine particles with polymers, waxes or greases. However, the softening temperatures of good coating materials are usually quite high. In order to avoid their displacement on storage or under regular use, therefore, it is desired to use coating materials that are of low viscosity at relatively low temperatures, at which they are applied, but after their application, it is desirable that their viscosity be much higher. Moreover, it is desired that the coating will be attracted specifically to the surfaces that are to be coated, prior to their curing process.

A recent Israeli patent application, IL 113283, filed April 6, 1995, by the same applicant herein, the description of which is incorporated herein by reference, discloses the use of certain carboxylic acid salts to improve the production of fine powders.

Another recent patent application, IL 114853, filed August 7, 1995, by the same applicant herein, the description of which is incorporated herein by reference,

discloses a novel method for modifying the surface charges of inorganic powders. The literature review in this patent application is also pertinent to the present invention.

Glass Fibers

Glass fibers are used extensively in reinforcing materials. However, their successful application is dependent on the ability to modify their surface properties and to transform the fibers into materials compatible with their surroundings. This is especially true when the glass fibers are to be applied in plastics as well as in cements. For instance, any attempt to use glass fibers to reinforce portland cement is doomed to fail, as the alkaline cements attack the glass and degrade the product (cf. - "Durability of E-Glass Fibre Reinforced Composites with Different Cement Matrices"; by K. Kolver and A. Bentur of the National Building Research Institute; the Technion - Israel Institute of Technology; Haifa; Israel and I. Odler of the Institute of Non-Metallic Materials; the Technical University-Clausthal; Clausthal; Germany).

Naturally, the problem raised above can be solved by a variety of methods, including those described in the article of K. Kolver et al, but the prior art is unable to furnish a simple, inexpensive and readily operable solution. Similar problems are encountered when using other reinforcing materials like fibers, whiskers and platelets of MgO , Al_2O_3 , SiC , TiN , etc.

Metal Powders

Metal powders are being used quite extensively in the plastics industry. However, their surfaces are not compatible with the hydrophobic plastics in which they are to be evenly distributed. Preparation of master batches of surface modified metallic powders by simply mixing the fine particles with melted polymers, waxes or greases has its drawbacks. These coatings should eventually exhibit high viscosity at the temperatures at which the metallic powders will be stored prior to their use, otherwise the coating will undergo dislocation or the fine particles will coalesce.

The quality of the coating adherence to the metallic surfaces is another problem that should be taken care of, while using simple and inexpensive methods and apparatus. The prior art uses powerful high shear mixers at elevated temperatures to obtain the desired products. However, this method is still quite limited to polymers of relatively low viscosity, it requires the use of heated equipment and it does not lead to sufficient adherence of the coating to the metal powders. Another approach to solving this problem is to increase the degree of polymerization of the coating while applying it on the desired surfaces. This approach is quite sophisticated and requires a very strict synchronization of the different steps in the process.

Slow Release Fertilizers

Recently, a patent application for a new production method of slow release fertilizers was filed by the present inventor (U.S. Patent Application Ser. No. 08/331,324, filed October 28, 1994), in which improved magnesite cements were used. This patent application also refers to publications that review the prior art of this technology of forming water soluble fertilizers coated with water insoluble materials.

Generally, such fertilizers are coated with, at least, two different layers as is manifested in EP 0276179, in which carboxylate salts are coated, in situ, on the respective fertilizers. Thereafter, a wax is coated onto the first layer. This second layer should either be applied at elevated temperatures, or the wax should be of a low melting range. This problem is particularly important when urea is to be turned into a slow-release fertilizer, since its low melting point does not allow the use of high melting waxes and, therefore, the second layer may lead to coalescence of the urea granules on storage under the harsh conditions at the storehouses and fields of the farms.

It is quite clear that the use of a wax of a low viscosity at a relatively low temperature, of the magnitude of the temperature at which the second coating layer is preferably produced, that can be turned later in the process into a high viscosity layer by simple and inexpensive methods, is highly desirable.

CaCO₃ Powders

A typical and most important example is powdered CaCO₃. Knowing the surface properties of calcite, and understanding how to modify them in order to improve its performance as a major filler in the plastics and the paper industries, are of prime importance. Efficient processes of surface coating of calcite with suitable polymers, waxes or greases, which may contain other fine powders like TiO₂ for improved brightness, Al for improved electrical and heat conduction, are still quite desired.

Mg(OH)₂ Powders

This material is used as a flame retardant in plastics and is a mild base. It may be produced by the hydrolysis of MgO in water. Performing the hydrolysis under conditions at which the surfaces of the raw material and the product are modified, may enhance the production rate substantially and allow the obtaining of powders that contain mainly single crystals that are already surface coated with fatty acid salts and/or polymers, waxes or greases. Operation of the surface coating of brucite can be done in a similar manner as in the abovementioned case of calcite.

Al(OH)₃ Powders

This material is used, among its other uses, as a flame retardant in plastics. It may be produced by the hydrolysis of Al₂O₃ in water. Performing the hydrolysis under conditions at which the surfaces of the raw material and the product are modified, may enhance the production rate substantially and allow the obtaining of powders that

contain mainly single crystals that are already surface coated with fatty acid salts and/or polymers, waxes or greases. Operation of the surface coating of the $\text{Al}(\text{OH})_3$ can be done in a similar manner as in the abovementioned cases of calcite and brucite.

The desire to turn hydrophilic surfaces of powder minerals into hydrophobic ones is general to a great many materials such as $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), $\text{Ca}(\text{OH})_2$, CaCO_3 , TiO_2 , Al_2O_3 , SiO_2 and CaSO_4 .

Surprisingly, it was found that the surfaces of organic and inorganic powders (e.g., metals like Al, Cu and Mn; natural and artificial minerals like MgO, talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , $\text{Ca}(\text{OH})_2$, Al_2O_3 , $\text{Al}(\text{OH})_3$, TiO_2 , SiO_2 , CaSO_4 ; fibers, whiskers and/or platelets of cellulose, glass, alumina, MgO, SiC, TiC, TiN; fertilizers like KNO_3 , KCl, K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, urea; organic and inorganic pigments like quinacridones, mineral oxides of iron or copper, etc.) can be coated at relatively low temperatures with "polymer solutions", which are liquids or waxy materials of low viscosity, and these coatings can then be turned into hard, high viscosity materials by simple chemical or physical interactions.

It is a purpose of the present invention to provide an inexpensive and simple method to produce fine powders, fibers, whiskers, platelets and/or granules that are coated with polymers, waxes or greases of high quality.

It is a further purpose of the invention to provide methods to improve these particles by coating them with suitable carboxylic acid salts and other additives.

It is a further purpose of the invention to provide methods to produce these coated particles using common and inexpensive raw materials and equipment.

It is further purpose of the present invention to demonstrate the uses of these coated particles, which are obtained by this novel coating method.

Other purposes and advantages of the invention will become apparent as the description proceeds.

Summary of the Invention

Surprisingly, it has been found that carboxylic acid solutions of sparingly water soluble polymers, waxes and/or greases like polyethylene (PE), polypropylene (PP), silicone rubbers, ethylene-acrylic acid copolymers, ethylene-maleic acid copolymers, ethylenevinylacetate copolymers and many others, which are extremely soluble in carboxylic acids at quite low temperatures, namely, at substantially lower temperatures than the softening point of the respective pure polymers, can be spread quite easily and economically, as thin or thick films, onto the surface of solids, especially onto the surface of fine powders. Furthermore, it has been found that these low viscosity liquids can then be altered to precipitate the high viscosity materials therein by simply transforming the carboxylic acids into the carboxylate forms by reacting them with suitable basic reagents, for example, aqueous solutions of ammonia and inorganic bases. Alternatively, the suitable carboxylic acids may be dissolved in an aqueous medium leading to the precipitation of the polymers onto the desired surfaces.

Note that, as used herein, the term "sparingly water soluble" means that the polymers, waxes, or greases used as coating materials are either insoluble or only slightly soluble in water.

This invention leads to the following major improvements over the prior art that is associated with coating of the hydrophilic surfaces of many fine powders with hard and adherent hydrophobic thin films of polymers, waxes or greases:

1. Spreading of the polymers can be done with simple mixers rather than with very powerful high shear mixers that are equipped with heating systems, as are required in the prior art.
2. The coating procedure can be carried out under relatively low temperatures, even at ambient temperature, while the polymers that are being used to coat the fine particles can be melted only at much higher temperatures. This allows the choosing of a larger variety of better suited polymers, i.e. with a quite higher softening temperature range, to coat materials of relatively low melting range. For instance, coating of urea granules with Epolene wax E-43 of Eastman Kodak is rather impossible without causing the particles of urea to melt (in this case the application of dissolved polymer in a suitable organic solvent is economically doomed). There is a rather large variety of materials that can, and should, be encapsulated with high melting waxes. However, this cannot be done unless the polymers are emulsified in water, or inert solvents are to be used. These must be recycled at the end of the process with high expenses and may cause the pollution of the environment and the product itself.
3. The precipitation of the polymers, and usually the precipitation of the respective carboxylate salts together with it, can be targeted towards pre-selected surfaces, that were surface-modified in advance according to the technology that is described in the aforementioned patent application (IL 114853), or according to any other suitable technology or surface treatment. This, in turn, may lead to substantial saving of the coating, as a thorough coverage is obtained with less polymers.

This invention is not at all limited to water or aqueous solutions. In some cases at which the surfaces of the powders to be coated are of basic nature (e.g. metals, metal oxides and metal hydroxides, and metal carbonates), the chemical reactions occur with the carboxylic acids in the absence of practically any solvent and lead the precipitation of the polymers, waxes and/or greases out of the polymer solution onto these active surfaces.

Organic solvents can (and should) be applied according to the present invention in cases as follows:

- a. The chemical properties of the coated powders forbid the use of aqueous media.
- b. The required quality of the resulting coating can not be obtained in a solventless operation or in aqueous media.

and naturally it is preferred that

- c. The economics of these operations (a. and b.), including recycling of the solvents, be viable.

The present invention, therefore, relates, inter alia, to a novel process for the coating of polymers, waxes and greases onto and/or in between inorganic and organic solids at a temperature that is usually much lower than the softening temperature of these original raw materials that constitute the coating.

The process of the invention is particularly important for the preparation of surface coated powders of inorganic materials such as Al, Cu, Mn, MgO, talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , $\text{Ca}(\text{OH})_2$, TiO_2 , Al_2O_3 , SiO_2 , CaSO_4 , $\text{Al}(\text{OH})_3$; fibers, whiskers and/or platelets of cellulose, glass, alumina, magnesia, ceramic carbides such as SiC and TiC, ceramic nitrides such as TiN, etc.; and mixtures thereof. Also, it is an important process for the preparation of surface coated free flowing fertilizers and especially of slow release fertilizers like KNO_3 , KCl, $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, urea, etc. and mixtures thereof.

The invention, inter alia, relates to a method for the production and uses of materials coated with polymers, waxes or greases. This invention makes it possible to produce powders of improved performance and compatibility with a variety of other materials, namely, minerals, plastics and cellulose, and lowers the cost of their production. This invention makes it also possible to glue two or more different materials together in an unconventional and inexpensive manner.

The present invention is particularly important in the fertilizers industry and in the production of powders for the cement (construction) industry, for the paper industry, for the cosmetics industry, for the adhesives industry, for the paint industry, for the ceramic industry, for the plastic and rubber industries, etc.

Detailed Description of Preferred Embodiments

The preparation of the "polymer solutions" by mixing suitable polymers, waxes and/or greases with suitable carboxylic acids can be easily done using simple mixers. The dissolution temperature may be below the softening temperature of the respective polymer, wax or grease, near it or above it. Naturally, it is preferred to produce the "polymer solutions" at ambient temperature, if that is possible, in order to save the cost of mixers with heating systems. The "polymer solutions" may be stored later at a temperature in the liquid state or below its pour point, as a soft paste. Another possibility is to prepare the desired polymers, in situ, by polymerising the respective monomers, dimers and/or oligomers in the carboxylic acid mixtures. A large variety of water insoluble or slightly water-soluble polymers, copolymers, block copolymers, grafted copolymers and mixtures thereof can be used in this invention.

The carboxylic acids may be applied in their acid form and/or their anhydride form and/or their acyl halide form. These forms are referred to herein collectively as "carboxylic compounds". The carboxylic compounds serve mainly as carriers for the

polymers, waxes and/or greases to be used for the coating. The forms to which these compounds are transformed chemically to precipitate the coatings onto the solid surfaces, i.e., carboxylates, esters and amides, are referred to herein collectively as "carboxylic derivatives". One should be aware of the fact that the anhydrides may be more reactive than the respective acids in aqueous solutions, in which they may be immersed in later applications. The acyl halides are more reactive and corrosive under certain conditions. Carboxylic acids containing one or more COOH groups may be used. However, the choice of the right acid should be made on a cost/performance basis. The longer the carbon chain of the carboxylic acid, the lower is its solubility in water.

The kind of cations that can be used when transforming the carboxylic acids, carboxylic acid anhydrides and/or carboxylic acid halides into the respective carboxylates may have a marked effect on the performance of the process and the quality of the final products - the coated objects. For instance, Al^{+++} , Ca^{++} and Mg^{++} may give rise to extremely water soluble salts of propionic acid, while these cations lead to salts of palmitic or oleic acids that are slightly soluble in water. Alkali and ammonium cations may lead to soaps, which in turn may assist in spreading the coating evenly onto the surface of the substrate. However, the choice of which carboxylic acids and/or of which cations to use can not be prescribed. It is worthwhile to note that, sometimes, mixing of various constituents may lead to a better cost/performance.

The carboxylic acids and/or carboxylic acid salts and/or the carboxylic acid anhydrides and/or the acyl halides may or may not have polymerized, in situ, during the production of the coating, or may have partially polymerized, in situ, during the production of the coated powders, and when they have polymerized they may be dimerized and/or oligomerized and/or polymerized in the presence or the absence of any added

polymerization initiators. The polymerization initiators, if added, are selected from among organic azo compounds and organic peroxide compounds, such as percarboxylates; inorganic peroxides, such as hydrogen peroxide, persulfates, percarbonates and perborates.

As mentioned above, the surface of the substrate may be pre-treated in order to target the coating onto the right surfaces and to effect chemical bonds of the coating with these surfaces.

The choice of the more suitable hydrophobic polymers, waxes or greases is within the scope of the skilled person, and in many cases, polymers of high softening temperatures and high viscosity are preferred. In other cases modified polymers, grafted with hydrophilic or hydrophobic groups, are used to obtain a better binding to the substrate surfaces. Mixtures of polymers can also be used, however, any one skilled in the art may find the optimal choices.

Other additives that are commonly used in the art are chosen from among organic and inorganic colorants and pigments. Of course, other conventional additives can also be added. In a preferred mode of operation, these additives may be pre-mixed with suitable carboxylic acids, with the "polymer solution"s and/or with the substrate that is to be coated.

Organic Solvents:

Though water and aqueous solutions offer outstanding economical and technological advantages in many applications, a large variety of organic solvents can be used to cause the precipitation the polymers, waxes and/or greases from the "polymer solution". Non-limiting examples are organic solvents, which are commonly grouped according to their functional groups, like hydrocarbons (saturated and unsaturated; cyclic and acyclic; linear and branched; halogenated - e.g. hexane, cyclohexane, toluene, xylene, etc.), alcohols (e.g. methanol, ethanol, 2-ethylhexylalcohol, etc.) aldehydes/ketones (e.g. propanal, acetone, 2-butanone, 2-hexanone, etc.), nitriles (e.g. acetonitrile, etc.), ethers (e.g. ethylether, monoglyme, diglyme, etc.), esters (e.g. ethylacetate, methylacetate, butylacetate, etc.), amides (e.g. dimethylformamide, dimethylacetamide, etc.) and/or sulphones/sulphoxides (e.g. sulfolane, dimethylsulphoxide, etc.). More than one solvent comprising one or more functional groups can be used (e.g. ethylene glycol, ethylene glycol monomethylether, diethylene glycol, etc.). Moreover, aqueous solutions of organic solvents may be used to reduce the surface tension or to achieve some special effects.

It is very common in organic chemistry and in the daily industrial practice, to assign the solvents, depending on their nature, into groups according to the following categories: polar/nonpolar and protic/aprotic. The properties of the various solvents consequently affect the kind of interactions with the carboxylic compounds and lead to the modification of the properties of the "polymer solutions" and to the precipitation of the polymers, waxes and/or greases:

polar/nonpolar solvents:

The polarity of the organic solvents may be affected by the kind of functional group(s) it carries and/or by the size of their hydrophobic hydrocarbon parts.

protic/aprotic solvents:

The nature of the functional group(s) of the organic solvents may be protic (able to donate a proton under the conditions of the application - e.g. alcohols, etc.) or aprotic (unable to donate a proton under the conditions of the application - e.g. ketones, nitriles, dimethylsulphoxide (DMSO), dimethylacetamide, etc.).

Under these categories toluene is considered a nonpolar/aprotic solvent and dimethylsulphoxide (DMSO) is considered a polar/aprotic solvent (note: water can be considered a polar/protic solvent). The protic solvents are distinct in their tendency to react with the carboxylic acid anhydrides and/or carboxylic acid halides, which may lead to the respective products, that are no longer able to act as carriers and dissolve the polymers, waxes and/or greases, thereby leading to their precipitation. For instance, alcohols react with carboxylic acid anhydrides and/or carboxylic acid halides and form the respective carboxylic acid esters. On the other hand alcohols (like water) may mix well with the carboxylic acids, altering their physical properties and leading to the formation of the desired coating. In most cases, amines may not be used as solvents, but rather as basic reagents. as they interact with the carboxylic acids, carboxylic acid anhydrides and/or carboxylic acid/halides to form carboxylic acid salts or amides, respectively. Acetone, dimethylsulphoxide, dimethylacetamide, and acetonitrile, which represent aprotic solvents, will only dissolve the suitable carboxylic acids, carboxylic acid anhydrides and/or carboxylic acid halides and cause the desired coating onto solids/powders.

Naturally, the use of such solvents requires their recycling and/or proper waste treatment. Such operations may be justified in cases at which the formed fine powders are expensive and/or there are no comparable alternative options to use water.

In some cases the water and/or organic solvents, with or without suitable reactants like acids or bases, may also cause chemical changes of the polymers, waxes and/or greases and their subsequent precipitation. However, that can be achieved very rarely without affecting the carboxylic compounds.

Surface active agents can be added to the "polymer solutions", to the solvents or can be formed by reacting suitable bases with the carboxylic acids, carboxylic acid anhydrides and/or carboxylic acid halides, as mentioned before.

In many cases the solids/powders to be coated by the polymers, waxes and/or greases are basic materials. In such cases contacting these solids/powders with the polymer solution may lead to a reaction with the carboxylic compounds and the precipitation of the polymers, waxes and/or greases onto their surfaces. In other cases the surfaces of the solids/powders to be coated can be turned basic prior to the application of the polymer solution (e.g. glass surface modified with fluorides and/or basic silicates), in order to initiate the reaction with the carboxylic compounds and to effect the precipitation of the polymers, waxes and/or greases. The phenomenon that was described above can be carried out in the presence or the absence of suitable solvents.

It should be noted that the precipitation of the polymers, waxes and/or greases out of the "polymer solutions" onto the solids/powders may be slow even when water or solvents are used. Therefore, it is possible to operate the coating process in quite different ways. For instance, the solid to be coated can be contacted first with the "polymer solution" and later with the solvent(s) and/or the suitable reagents, it can be contacted first with the solvent(s) and/or the reagents and later with the "polymer solution", it can be contacted with a mixture of the "polymer solution" and the solvent(s) and/or the reagents in a coating process in which all the components are added simultaneously or it can be contacted with a mixture of the "polymer solution" and the solvent(s) and/or the reagents, that were mixed together and maintained under

agitation quite a short time prior to the application. This short time mentioned above is optimally defined as the time that the precipitation process of the polymers, waxes and/or greases still take place.

A particularly important mode of operation are the continuous (and semicontinuous) processes, at which the fine particles of the product are formed and are being coated, simultaneously in situ, by polymers, waxes and/or greases that precipitate all along. An non-limiting example of such a process is the production of PCC (precipitated calcium carbonate) at which the slurry of calcium hydroxide, the "polymer solution" and the carbon dioxide are fed simultaneously into a flotation cell.

There are numerous options to operate this novel technology. Therefore, the optimal operation, in each case, may be achieved by the person skilled in the art.

All the above and other characteristics and advantages of the invention will be better understood through the following illustrative and non-limitative description of preferred embodiments.

Experimental Data**Raw Materials****Carboxylic acids or Fatty Acids**

-Propionic Acid of Aldrich	-FA-1
-Caprylic Acid of Aldrich	-FA-2
-Capric Acid of Aldrich	-FA-3
-2-Ethylcaproic Acid of Aldrich	-FA-4
-Tall oil of Arizona Chemical Co.	-FA-5
-Lauric Acid of Aldrich	-FA-6
-Palmitic Acid of Aldrich	-FA-7
-Oleic Acid of Aldrich	-FA-8
-Valeric Acid of Aldrich	-FA-9
-Nitrilotriacetic Acid (NTAH ₃) of Aldrich	-FA-10
-Phthalic Anhydride of Fluka	-FA-11
-Maleic Anhydride of Fluka	-FA-12
-2-Ethylhexanoyl Chloride of Aldrich	-FA-13

Polymers, Waxes and Greases

-Polyethylene of Allied Signal, Grade 6-A	-POL-1
-Polyethylene Acrylic Acid Copolymer of Allied Signal, Grade 540-A	-POL-2
-Polyethylene Grease of Allied Signal, Grade 1702	-POL-3
-Polyethylene Acrylic Acid Copolymer of Allied Signal, Grade 5180	-POL-4
-Epolene Wax of Eastman Kodak, Grade E-43	-POL-5
-LDPE of Carmel Olefines, Grade Ipethene-900	-POL-6

Organic SolventsSaturated and Unsaturated Hydrocarbons

- Toluene of Aldrich
- Hexane of Aldrich
- Cyclohexane of Aldrich

Alcohols

- Ethanol of Aldrich
- Diethyleneglycol of Aldrich

Aldehydes/ketones

- Acetone of Aldrich
- Ethylmethylketone of Aldrich

Ethers

- Diglyme of Aldrich
- Monoglyme of Aldrich

Esters

- Ethylacetate of Aldrich

Nitriles

- Acetonitrile of Aldrich

Amides

- Dimethylacetamide of Aldrich

Sulphones/Sulphoxides

- Sulfolane of Aldrich
- Dimethylsulphoxide of Aldrich

Inorganic Materials

- Calcined MgO, a product of Grecian Magnesite grade "Normal F" - "MgF"
- Glass Fibers of Owen-Corning of Diameter of 10-13 Microns and Nominal Length $L=4.5$ mm
- Calcium Hydroxide (Ca(OH)_2) of Frutarom
- Potassium Sulfate (K_2SO_4) of Frutarom
- Potassium Chloride (KCl) of Frutarom
- Mono Ammonium Phosphate (MAP) of Aldrich
- Triple Super Phosphate (TSP) of Rotem Fertilizers Ltd
- MgSO_4 solution having a density of $d=1.2 \text{ g/cm}^3$ where the ratio $\text{H}_2\text{O/MgSO}_4 =$

3.1

- MgCl_2 solution having a density of $d=1.267-1.27 \text{ g/cm}^3$ where the ratio $\text{H}_2\text{O/MgCl}_2=2.61$
- CaCO_3 powder ($d_{50}=5$ microns) of Polychrom. Israel- "Girulite-10"
- CaCO_3 powder ($d_{50}=18$ microns) of Polychrom, Israel- "Girulite-40"
- Sodium Silicate Solution (14% NaOH and 27% SiO_2) of Fluka
- Ferric Chloride (FeCl_3) of Riedel-de Haen
- Ferrous Sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) of Riedel-de Haen
- Aluminum (Al) metal powder of Moniplet & Estban S.A, Spain- Grade Panreac/P.R.S

Raw materials of high purity are not of prime importance. Commercially available materials can be used.

Example 1**Preparation of Polymer Solutions in Carboxylic Acid(s)**

A glass beaker equipped with a magnetic stirrer, a heater and a thermometer was used to dissolve polymers, greases and waxes in carboxylic acids and/or carboxylic acid anhydrides and/or carboxylic acid halides. The dissolution was conducted at a temperature range much below the softening temperatures of the corresponding polymers, greases and waxes during up to 30 mins.. Clear and transparent liquids of relatively low viscosity were obtained. Several examples are given in Table 1 below:

Table 1

Test #	Type of Carboxylic Acid	Type of Carboxylic Acid	Type of Polymer	Load of Polymer % (wt)	Temperature °C
1	Propionic	FA-1	POL-3	30	30
2	Caprylic	FA-2	POL-4	40	30
3	Capric	FA-3	POL-1	35	40
4	2-Ethylcaproic	FA-4	POL-4	45	35
5	Valeric	FA-9	POL-2	35	40
6	Tall Oil	FA-5	POL-5	30	25
7	Lauric	FA-6	POL-5	30	50
8	Palmitic	FA-7	POL-5	30	70
9	Oleic	FA-8	POL-5	60	25
10	Palmitic	FA-7	POL-6	35	70
11	Tall Oil	FA-5	POL-6	30	50
12	Oleic	FA-8	POL-6	30	50
13	Phthalic Anhyd.	FA-10	POL-5	25	140
14	Maleic Anhyd.	FA-11	POL-5	25	60
15	2-Ethylhexanoyl Chloride	FA-12	POL-6	20	60

Remarks:

1. Acids, acid anhydrides and also acyl halides.

2. The viscosity of the solutions may be increased by e.g. reducing the temperature or by increasing the polymer concentration. Depending on the specific combinations (e.g. polymers and acids) and the relative concentrations of the constituents, soft and stable pastes can be obtained at ambient temperatures.

Example 2**Production of Surface Coated $\text{Mg}(\text{OH})_2$ Fine Powder**

Surface coated $\text{Mg}(\text{OH})_2$ fine powder was obtained in the following manner:

Raw Materials Per One Batch

- 100g calcined MgO
- 100g water at 50°C
- 1.5g propionic acid (FA-1)
- 2.0g MgSO_4 brine
- 2.0g solution of tall oil (FA-5) + Epolene wax (POL-5) (80% (wt) and 20% (wt), respectively)

The warm water and the MgO were introduced into a beaker (cf. - Example 1). The slurry was stirred and the temperature was kept at 50°C during the test. Then, the other reagents were added simultaneously to the stirred slurry and the mixture was allowed to stir for a total duration of 40 mins.. The slurry was then filtered off (the pH of the supernatant was in the range of 9.5-10); the solid was dried for 15hrs. in an oven at 110°C ; the dry cake was disintegrated into a fine powder.

The fine powder was subjected to the following tests:

1. XRD revealed that the product is brucite ($\text{Mg}(\text{OH})_2$).
2. SEM revealed hexagonal crystals of 0.5 micron (average).
3. Flotability test using Modified Halimond Tube (a well known floatability tests - cf. "Mineral Processing"; E. J. Pryor; Third Ed.; Elsevier Publishing Co.; 1965; pp. 463-468) revealed 100% surface coated product (namely, hydrophobic brucite fine particles).

Example 3

A. Production of Surface Coated Glass Fibers in Water

Surface coated glass fibers were obtained in the following manner:

Raw Materials Per One Batch

- 100g glass fibers
- 550g water at 50°C
- 0.5g sodium silicate solution
- 2.0g MgSO₄ brine
- 3.0g polymer solution of oleic acid (FA-5) + Epolene wax (POL-5) (80% (wt) and 20% (wt), respectively)
- 0.5g calcined MgO

The warm water and the glass fibers were introduced into a beaker (cf. - Example 2). The sodium silicate solution and the MgSO₄ brine were added to the stirred mixture after 10 mins. and it was allowed to stir for additional 2 mins. (the pH of the mixture was then at ~9). The polymer solution was added and the mixture was allowed to stir for additional 6 mins. The MgO was then added and the mixture was allowed to stir for additional 2 mins.. The whole experiment was carried out at 50°C.

The glass fibers were filtered off and dried in a oven at 110°C for 15 hrs..

The dry cake was subjected to a flotability test using Modified Halimond Tube (a well known floatability test - cf. "Mineral Processing"; E. J. Pryor; Third Ed.; Elsevier Publishing Co.; 1965; pp. 463-468) which revealed 100% surface coated product (namely, hydrophobic glass fibers).

B. Production of Surface Coated Glass Fibers in Organic Solvents

Surface coated glass fibers were obtained in the following manner:

Raw Materials Per One Batch

-100g glass fibers

-550g organic solvent

-3.0g polymer solution of propionic acid (FA-1) + Epolene wax (POL-5) (80% (wt) and 20% (wt), respectively)

The organic solvent and the glass fibers were introduced into a beaker (cf. - Example 2). The mixture was allowed to stir for additional 10 mins.; the polymer solution was added and the mixture was allowed to stir for additional 5 mins. The whole experiment was carried out at 30°C.

The glass fibers were filtered off and dried in a vacuum oven (30 mm Hg) at 100°C for 15 hrs..

The dry cake was subjected to a flotability test using Modified Halimond Tube (a well known floatability test - cf. "Mineral Processing"; E. J. Pryor; Third Ed.; Elsevier Publishing Co.; 1965; pp. 463-468) which revealed 100% surface coated product (namely, hydrophobic glass fibers).

The following solvents were used: ethanol; diethyleneglycol, monoglyme, diglyme, acetonitrile; acetone; ethylmethylketone; ethylacetate; dimethylsulphoxide; sulfolane.

The experiment was repeated with another polymer solution:

-3.0g polymer solution of oleic acid (FA-5) + Epolene wax (POL-5) (80% (wt) and 20% (wt), respectively).

The following solvents were used: hexane; cyclohexane; toluene; acetonitrile; acetone; ethylmethylketone; ethylacetate.

The results obtained were practically similar to those obtained above.

Example 4**Production of Surface Coated Calcium Carbonate**

CaCO₃ powder (d₅₀=5 microns) of Polychrom, Israel- "Girulite-10" were coated by several polymer solutions as follows:

400g calcium carbonate and 200g water were mixed in a Retch KM-1 mixer and the following materials were introduced:

1. Ca(OH)₂ powder until the pH reached the range of 9.0-9.5
2. 4g MgSO₄ brine
3. A polymer solution, as specified in Table 2:

Table 2

Test #	Weight (g)				Type of Material	
	CaCO ₃	Water	FA	POL	FA	POL
16-	400	200	4.0	1.0	1	3
17	400	200	4.0	1.0	2	4
18	400	200	3.0	1.0	7	5
19	400	200	3.0	1.0	5	5
20	400	200	3.0	1.0	6	5
21	400	200	30.0	100.0	8	6

The slurry was further mixed for 5 mins. The products were then filtered off and dried at 110°C for 15 hrs. The dry products were disintegrated to powders and subjected to the Modified Hallimond Tube test (a well known floatability tests - cf. "Mineral Processing"; E. J. Pryor; Third Ed.; Elsevier Publishing Co.; 1965; pp. 463-468) to check the quality of coating obtained. All the sample tested were found to be 100% hydrophobic.

Example 5**Production of Slow Release Fertilizers**

Granules of slow release fertilizers were prepared in three stages as follows:

1. Mixing the fertilizers and other additives in order to produce granules in order to produce magnesite cement coated material.
2. Granulation of the above material (of stage 1) and sieving to obtain granulated fertilizers of the size of +3.5-2.0 mm.
3. Coating the granules (of stage 2) with polymer solutions and hardening it.

Stage 1

The first stage was conducted in a laboratory mixer - Retch type KM-1. The materials described in Table 3 and Table 4 constituted the product of this stage:

Table 3

Test #	Fertilizer	Composition
22	250g K ₂ SO ₄ +	10g Urea
23	200g KCl +	50g TSP
24	220g MAP +	30g TSP

Table 4

Test #	Weight (g)								
	Fertilizer	MgCl ₂	MgSO ₄	CaCO ₃ ⁽¹⁾	FeCl ₃	FeSO ₄ ⁽²⁾	NTAH ₃	Water	MgO
22	260		20	25		5	0.6	5	25
23	250	25		20	20		0.6	9	20
24	250		20	20		10	0.6	10	25

Remarks:

(1) CaCO₃ powder (d₅₀=18 microns) of Polychrom, Israel- "Girulite-40"

(2) FeSO₄·7H₂O was used

Stages 2 & 3

The products of the above stage were sieved and the desired granules were coated by spraying them with the suitable polymer solutions in a rotating granulating pan. Thereafter, the granules were dusted with a fine powder of MgO in the granulator, where the chemical reaction with the corresponding carboxylic acid(s) led to the precipitation of the carboxylate salt(s) and the polymer onto the surface of the fertilizer. The surface of the granules became immediately hard and the products were ready for packaging. However, the magnesite cement continued to cure for an additional 7 days. The polymer solutions that were applied (containing 80% (wt) carboxylic acid and 20% (wt) polymer) are given in Table 5:

Table 5

Test #	100g Granules of Fertilizer from Test #	Polymer Solution (g)	The Composition of the Polymer Solution	MgO (g)
25	22	8	Tall Oil Acid + Epolene Wax	2.0
26	22	10	Oleic Acid + LDPE	2.0
27	24	6	Oleic Acid + Epolene Wax	2.0
28	24	8	Palmitic Acid + Epolene Wax	2.0
29	25	8	Tall Oil Acid + Epolene Wax	2.0
30	25	10	Tall Oil Acid + LDPE	2.0

The third stage comprised the evaluation of the resulted fertilizers as follows:

The coated and hardened fertilizers of the previous stage were immersed in water (1:10 wt ratio) at 22°C. After 5 days the water was removed from the wet fertilizers, which were then dried at 70°C for 24 hrs. The results are given in Table 6, which contains also comparison tests of uncoated fertilizers:

Table 6

Test #	Fertilizer Taken From Test #	$W_0^{(1)}$ (g)	$W_{5 \text{ Days}}^{(2)}$ (g)	% Weight Loss	Note
31	22	20	15.0	25.0	Reference
32	23	20	13.0	35.0	Reference
33	24	20	14.0	30.0	Reference
34	25	20	19.8	1.0	Coated Product
35	26	20	19.5	2.5	Coated Product
36	27	20	19.0	5.0	Coated Product
37	28	20	18.5	7.5	Coated Product
38	29	20	19.0	5.0	Coated Product
39	30	20	19.0	5.0	Coated Product

Remarks:

(1) The initial weight of the fertilizer in the test.

(2) The weight of the dry fertilizer after 5 days in water.

Example 6**Production of Metal Coated Polymers****Raw Materials**

-500g LDPE (POL-6)

- 4g polymer solution (containing: 3g tall oil acid + 1g Epolene wax)
- 1g aluminum metal powder
- 1g MgO powder

The LDPE granules were rotated in a granulating pan. Then, the polymer solution was sprayed onto the LDPE to form a thin adherent layer. Thereafter, the coated granules were dusted with the aluminum powder to form a homogeneous metal coating.

Eventually, the MgO fine powder was dusted on top of the granules, which caused the immediate hardening of the coated layer.

At this stage, evenly coated LDPE granules with aluminum were obtained and any attempt to wipe off the aluminum powder from the granules was futile.

All the above description and examples have been provided for the purpose of illustration and are not intended to limit the invention. Many modifications can be effected in the various procedures, processes and additives, to give a variety of surface-modified minerals, all without exceeding the scope of the invention.

CLAIMS

1. A process for coating a solid with a sparingly water soluble coating, comprising the steps of:
 - (a) selecting at least one coating material from the group consisting of high viscosity polymers, waxes, and greases;
 - (b) dissolving said at least one coating material in a carrier including at least one carboxylic compound selected from the group consisting of carboxylic acids, carboxylic acid anhydrides, and carboxylic acid halides, thereby creating a polymer solution;
 - (c) contacting the solid with said polymer solution; and
 - (d) precipitating said at least one coating material onto the solid.
2. The process of claim 1, wherein said precipitation is effected chemically.
3. The process of claim 2, wherein said precipitation is effected by transforming at least one of said at least one carboxylic compound into a carboxylic derivative.
4. The process of claim 1, wherein said precipitation is effected physically.
5. The process of claim 4, wherein said precipitation is effected by dissolving said carrier.
6. A process for producing a powder with a sparingly water soluble coating, comprising the steps of:

- (a) selecting at least one powdered material;
- (b) selecting at least one coating material from the group consisting of sparingly water soluble polymers, sparingly water soluble greases, and sparingly water soluble waxes;
- (c) dissolving said at least one coating material in a carrier including at least one carboxylic compound selected from the group consisting of carboxylic acids, carboxylic acid anhydrides, and carboxylic acid halides, thereby producing a polymer solution; and
- (d) contacting said at least one powdered material with said polymer solution.

7. The process of claim 6, further comprising the step of precipitating said at least one coating material onto said at least one powdered material.

8. The process of claim 7, wherein said precipitation is effected chemically.

9. The process of claim 8, wherein said precipitation is effected by converting said at least one carboxylic compound into a carboxylic derivative.

10. The process of claim 9, wherein said conversion is effected by reacting said at least one carboxylic compound with at least one reagent.

11. The process of claim 10, wherein said at least one reagent is selected from the group consisting of water, ammonia, inorganic bases, alcohols, and amines.

12. The process of claim 7, wherein said precipitation is effected physically.

13. The process of claim 12, wherein said precipitation is effected by dissolving said carrier in at least one solvent.

14. The process of claim 13, wherein said at least one solvent is selected from the group consisting of water, linear saturated hydrocarbons, linear unsaturated hydrocarbons, branched saturated hydrocarbons, branched unsaturated hydrocarbons, cyclic saturated hydrocarbons, cyclic unsaturated hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, aldehydes, ketones, ethers, esters, amides, nitriles, sulphones, and sulfoxides.

15. The process of claim 6, wherein said at least one powdered material is selected from the group consisting of metals, minerals, ceramics, cellulose, glass, fertilizers, and pigments.

16. The process of claim 15, wherein said metals include aluminum, copper and manganese.

17. The process of claim 15, wherein said minerals include MgO, talc, $\text{Mg}(\text{OH})_2$, CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , $\text{Ca}(\text{OH})_2$, Al_2O_3 , $\text{Al}(\text{OH})_3$, TiO_2 , SiO_2 , CaSO_4 , SiC, TiC and TiN.

18. The process of claim 17, wherein said Al_2O_3 , said MgO, said SiC, said TiC and said TiN are characterized by a physical form selected from the group consisting of fibers, whiskers, and platelets.

19. The process of claim 15, wherein said cellulose and said glass are characterized by a physical form selected from the group consisting of fibers, whiskers, and platelets.
20. The process of claim 15, wherein said ceramics include oxides, carbides, and nitrides.
21. The process of claim 15, wherein said fertilizers include KNO_3 , KCl , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and urea.
22. The process of claim 15, wherein said pigments include quinacridones, oxides of iron, and oxides of copper.
23. The process of claim 15, wherein said at least one solid material is $\text{Mg}(\text{OH})_2$.
24. The process of claim 15, wherein said at least one solid material is MgO .
25. The process of claim 15, wherein said at least one solid material is CaCO_3 .
26. The process of claim 15, wherein said at least one solid material is $\text{Ca}(\text{OH})_2$.
27. The process of claim 15, wherein said at least one solid material is Al_2O_3 .

28. The process of claim 15, wherein said at least one solid material is $\text{Al}(\text{OH})_3$.
29. The process of claim 15, wherein said at least one solid material is TiO_2 .
30. The process of claim 6, wherein said at least one powdered material is a water soluble fertilizer.
31. The process of claim 30, wherein said at least one powdered material is selected from the group consisting of KNO_3 , KCl , $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, and urea.
32. The process of claim 6, wherein said at least one powdered material is a metal.
33. The process of claim 32, wherein said at least one powdered material is selected from the group consisting of aluminum, copper, and manganese.
34. The process of claim 6, wherein said at least one powdered material is characterized by a physical form selected from the group consisting of fibers, whiskers, and platelets, and wherein said at least one powdered material is selected from the group consisting of glass, alumina, magnesia, and ceramic materials.
35. The process of claim 34, wherein said at least one powdered material is selected from the group consisting of SiC , TiC , and TiN .

36. The process of claim 6, wherein said at least one powdered material is a pigment.

37. The process of claim 36, wherein said at least one powdered material is selected from the group consisting of quinacridones and metal oxides.

38. The process of claim 37, wherein said at least one powdered material is selected from the group consisting of iron oxides and copper oxides.

39. The process of claim 6, wherein said at least one coating material is selected from the group consisting of paraffins, long chain fatty acid esters, silicone rubbers, polymers, polyolefins, copolymers of polyolefins, and grafted copolymers of polyolefins.